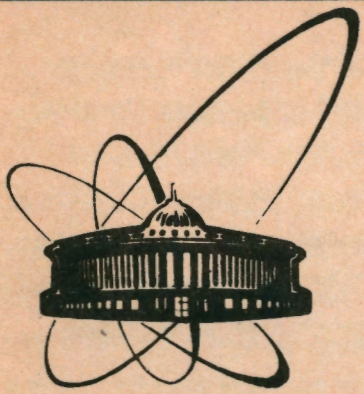

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A DYNAMICAL MODEL OF STRUCTURAL PHASE TRANSITION IN La_2CuO_4

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1. Introduction

Since the discovery of HTSC [1] special attention has been given to the structural phase transition (SPT) in perovskite-like compounds: $La_{2-x}M_xCuO_4$(M=Sr,Ba,Ca). It has been shown (see[2-4]) that SPT from the tetragonal D_{4h}^{17} (HTT) to orthorhombic D_{2h}^{18}(LTO) phase is caused by condensation of the rotational tilting mode with wave vectors: $\vec{q}_1=\pi/a(1,1,0)$ $\vec{q}_2=\pi/a(-1,1,0)$ at the temperature of SPT T_0. The latter drops rapidly as the concentration of impurities increases, $T_0(x)\approx T_0(1-ax)$ [5,6].

At the same time, another SPT was observed in $La_{2-x}Ba_xCuO_4$ (at $T_0<60K$ for $0,05<x<0,2$) at which the system undergoes transition to a low temperature tetragonal D_{4h}^{16}(LTT) phase [7,8]. Investigation of the superconducting properties for these compounds have revealed an abrupt decrease of superconductivity temperature T_c, and anomalous behavior of the thermoelectric power and Hall effect at $x \cong 0,12$. Also the anomalous increase of isotopic effect was observed in $La_{2-x}Sr_xCuO_4$ in the same region of concentration for the LTT phase, $\alpha=0,6$ at $x=0,12$ [9]. These results indicate correlation between structural anomalies and superconductivity. The highly anharmonic character of the lattice vibrations was observed in inelastic neutron scattering [10]. A strong softening of some of the elastic constants at SPT, which implies the interection between strains and the soft mode was also observed [11,12].

Investigations of the SPT HTT⟶LTO in the framework of the microscopical model have been proposed in [13]. The vibrations in the local normal coordinates were considered. However, only oxygens in CuO_2 plane were taken into account explicitly while the

apical oxygen vibrations were considered by means of renormalization of the momentum of inertia.

In this letter a generalization of the model [13] is proposed where apical oxygen vibrations and their interactions with strains are taken into account explicitly. The model parameters are estimated by microscopical calculations of the potential energy of the crystal[18] and by using measurements of the elastic coefficients in acoustic studies [12].
It is shown that the consideration the apical oxygens is important for determining the sequence of phase transitions HTT-→LTO-→LTT. For the calculated model parameters at x=0 the HTT-→LTO, phase transition is realized. To describe the other phase transition HTT→LTT, a strong x-dependece of the anharmonic constants , especially for the apical oxygens , should be introduced [14].

2. The Model Hamiltonian

The total anharmonic Hamiltonian of the LCO compound is written in the form:

$$H = H_R + H_c + H_{R-c} \tag{1}$$

$$H_R = \frac{m}{2}\sum_{l,k}\dot{u}_\alpha^2(l,k) + \frac{1}{2}\sum_{ll',kk'}\Phi_{kk'}^{\alpha\beta}(l-l')\,u_\alpha(l,k)\,u_\beta(l',k') +$$
$$+B_0\,\frac{1}{4}\sum_{l,k=1,2}u_z^4(l,k) + B_1\,\frac{1}{4}\sum_{l,k=3,4}[u_x^4(l,k)+u_y^4(l,k)] + \tag{2}$$
$$+B_2\,\frac{1}{2}\sum_{l,k=3,4}u_x^2(l,k)u_y^2(l,k)$$

where $u_\alpha(l,k)$ is an α-th component of the ion displacements of oxygen where k=1,2 stands for atoms in the plane CuO_2, and k=3,4 for the apical oxygen, m is the oxygen mass, $\Phi_{kk'}^{\alpha\beta}(l-l')$ is the harmonic force constant, B_0, B_1, B_2 are the constants of a local anharmonic interaction. In the Hamiltonian (2) only displacements of the

oxygen ions in the soft mode are taken into account. This mode is related to the rigid rotation of the CuO_6 octahedron as a whole in the LMCO lattice. By taking into account of oxygen position the in teraction of the ion displacements in the soft mode with strains can be written as:

$$H_R = \sum_1 \varepsilon_{\alpha\alpha}(1) \Big[\sum_{k=1,2} u_z^2(1,k)\big(g_{33}\,\delta_{\alpha 3} + g_{13}\,\delta_{\alpha k} + g_{23}(1-\delta_{\alpha k})\big) + \sum_{k=3,4} u_\beta^2(1,k)\big(g_{31}\delta_{\alpha 3} + g_{11}\delta_{\alpha\beta} + g_{12}(1-\delta_{\alpha\beta})\big)\Big] + \sum_{1,k=3,4} \varepsilon_{xy}(1)\, u_x(1,k)\, u_y(1,k)\, g_{66} \qquad (3)$$

Because of the tetragonal symmetry of the lattice for $T>T_0$ there exist seven independent components of $g_{\mu\nu}$. $\varepsilon_{\alpha\beta}(1,k)$~ $\varepsilon_{\alpha\beta}(1)$ is the static deformation taken into consideration in the long-wavelength limit. The potential energy of the distorted lattice takes the form:

$$H = \tfrac{1}{2} \sum_{\mu\nu} C_{\mu\nu}\varepsilon_\mu\varepsilon_\nu \qquad (4)$$

To describe the displacements of oxygen ions in the soft tilting mode we introduce the local normal coordinates $R_\lambda(1)$ related to the rotation of the CuO_6- octahedra [15-16]:

$$u_z(1,k) = \frac{1}{2\sqrt{2m}}\, e_{z\lambda k}\big[R_\lambda(\vec{1}+a\vec{\xi}) - R_\lambda(\vec{1})\big] \qquad (5)$$

where for plane atoms k=1,(2). Local normal coordinates $R_\lambda(1)$ describe the rotation of octahedra around the axes $\lambda=y(x)$, a is the lattice constant, $\vec{\xi}_1=(1,1,0)$, $\vec{\xi}_2=(-1,1,0)$, $e_{\alpha\beta\gamma}$ is the antisymmetric tensor. For apical ions (k=3,4)we have:

$$u_\alpha(1,k) = \frac{1}{\sqrt{2\tilde{m}}}\, e_{\alpha\lambda 3}\, R_\lambda(1) \qquad (6)$$

where $\lambda=x(y)$ for $\alpha=y(x)$ and $\tilde{m}=m(d_\lambda/d_z)^2$ is the effective mass of the apical oxygen atoms, $d_x = d_y = a/2$ and d_z are distances between

the copper and plane and apical oxygen ions, respectively. In view of the definition of local normal coordinates (5),(6) the Hamiltonian (1) can be written as:

$$H = \tfrac{1}{2}\sum_{11'}\sum_{\lambda} I_{\lambda\lambda}(1,1')\, \dot{R}_\lambda(1)\dot{R}_\lambda(1') + \tfrac{1}{2}\sum_{11'}\sum_{\lambda\lambda'} V_{\lambda\lambda'}(1-1')R_\lambda(1)R_{\lambda'}(1') + \tfrac{1}{4}\sum_{11'}\sum_{\lambda} \Gamma_{\lambda\lambda}(11')[R_\lambda(1)-R_\lambda(1')]^4 + \tfrac{1}{4}\sum_{1\lambda}\Gamma_1 R_\lambda^4(1) + \tfrac{1}{2}\sum_{1\lambda}\sum_{\lambda\neq\lambda'}\Gamma_2 R_\lambda^2(1)R_{\lambda'}^2(1) + \sum_{11'}\sum_{\lambda\neq\lambda'}\big[G_{23}\varepsilon_{\lambda\lambda} + G_{13}\varepsilon_{\lambda'\lambda'} + G_{33}\varepsilon_{zz}\big]\gamma_\lambda(11')R_\lambda(1)R_\lambda(1') + \sum_{1\lambda}\sum_{\lambda'\neq\lambda}\big[G_{12}\varepsilon_{\lambda\lambda} + G_{11}\varepsilon_{\lambda'\lambda'} + G_{31}\varepsilon_{zz}\big]R_\lambda^2(1) + \sum_1 G_{66}\varepsilon_{xy}R_x(1)R_y(1) + H_\varepsilon \qquad (7)$$

where $I_{\lambda\lambda}(11') = \frac{1}{2}\frac{1}{N}\sum_q e^{iq(1-1')}\big[(1-\cos q_\lambda a)+(d_z/d_\lambda)^2\big]$ is the nonlocal momentum of inertia and $V_{\lambda\lambda'}(1-1')$ is the harmonic force constant matrix. $\gamma_\lambda(11') = \frac{1}{N}\sum e^{iq(1-1')}(1-\cos q_\lambda a)$, and $\Gamma_{\lambda\lambda}(11') = \frac{1}{N}\sum_q \Gamma_0 e^{iq(1-1')}\cos q_\lambda a$.

$$\Gamma_0 = \frac{1}{64\,m^2}B_0,\quad \Gamma_1 = \frac{1}{4\,\tilde{m}^2}B_1,\quad \Gamma_2 = \frac{1}{4\,\tilde{m}^2}B_2$$

$$G_{\nu 3} = \frac{1}{2\,m}g_{\nu 3},\quad G_{\nu\mu} = \frac{1}{2\,\tilde{m}}g_{\nu\mu},\ (\nu\neq 3). \qquad (8)$$

To describe the soft tilting mode we introducethe local normal coordinates:

$$R_{1,2}(1) = \frac{1}{\sqrt{2}}\,[R_y(1) \pm R_x(1)] \qquad (9)$$

Condensation of these rotations for $T<T_0$ leads to static displacements:

$$\langle R_s(1)\rangle = Q_s e^{iq_s l} \qquad (10)$$

where $\vec{q}_S=(\vec{q}_1,\vec{q}_2)$ is a two-armed star of the wave vector at the X-point of the BZ and $Q_S(T)/Q_S(0)=\eta_s$, (s=1,2)is a dimensionless order-parameter, $|\eta_S|<1$. Furthermore, the frequency of the soft mode in the harmonic approximation is unstable:

$$\omega_1^2(q_1)=\omega_1^2(q_2)<0 \qquad (11)$$

3. The free energy and phase transition

Let us evaluate the free energy of the model(7) by using the pseudoharmonic approximation [17].To this end we introduce the trial Hamiltonian of the system:

$$H_0=\frac{1}{2}\sum_{ss'q} I(q) r_s(-q) r_{s'}(q) + \frac{1}{2}\sum_{ss'q}\varphi_{ss'}(q)\, r_s(-q)\, r_{s'}(q) \qquad (12).$$

where $r_s(q)=R_s(q)-\langle R_s(q)\rangle$. Applying the variational method for Hamiltonian (7) we have:

$$F=F_0+\langle H-H\rangle_0 ,\quad F_0=-T\ln[Sp\{e^{-H_0/T}\}] \qquad (13)$$

Using the variational condition for the trial dynamical matrix (see[18]):

$$\varphi_{ss'}(q)=2\,\delta F_1/\delta\langle r_s(-q)r_{s'}(q)\rangle = 2\,\delta\langle H\rangle_0/\delta\langle r_s(-q)r_S(q)\rangle$$

we get the following expression for the eigenfrequency of the soft mode:

$$\Omega_s^2(q_s,T)=\varphi_{ss}(q_s,T)=\omega_s^2(q_s)+[24\,\Gamma_0+\tfrac{3}{2}\Gamma_1+\tfrac{3}{2}\Gamma_2][Q_s^2+\Delta_s(T)]+$$
$$+[24\,\Gamma_0+\tfrac{3}{2}\Gamma_1-\tfrac{1}{2}\Gamma_2][Q_\nu^2+\Delta_\nu(T)](1-\delta_{s\nu})+L_{ss}(q_s). \qquad (14)$$

where $\Delta_s(T)=\frac{1}{N}\sum_k\sum_q\gamma_k(q)\langle r_s(-q)r_s(q)\rangle =$

$$=\frac{1}{N}\sum_{\mu,k}\sum_q\gamma_k(q)e^s_\mu(q)e^s_\mu(q)\frac{1}{2\,\Omega_\mu(q)}\,\mathrm{cth}\,\frac{\Omega\mu(q)}{2\,T}.$$

The quantities $\Gamma_0,\Gamma_1,\Gamma_2$and $\omega^2(q_s)$are determined in (8),(11)respectively.The matrix $L_{ss'}(q_s)$ is the strain contribution to the soft mode .The SPT temperature is determined by the equation:

$$\Omega_s^2(q_s T_0)=0 .$$

Writing now the free energy (13):

$$\frac{1}{N}F_1=\frac{1}{2}\omega^2(q_s)(Q_1^2+Q_2^2)+u(Q_1^2+Q_2^2)^2+v(Q_1^4+Q_2^4)+ \qquad (15)$$
$$+\{\alpha\sum_\lambda\varepsilon_{\lambda\lambda}+\beta\,\varepsilon_{zz}\}(Q_1^2+Q_2^2)+\gamma\varepsilon_{xy}(Q_1^2-Q_2^2)+F_\varepsilon+V_{fl}$$

where $\alpha=G_{13}+G_{23}+G_{11}+G_{12}$, $\beta=G_{33}+G_{31}$, $\gamma=G_{66}$, $u=6\Gamma_0+\frac{3}{8}\Gamma_1-\frac{1}{8}\Gamma_2$, $v=\frac{1}{4}\Gamma_2-4\Gamma_0-\frac{1}{4}\Gamma_1$ and V_{fl} is fluctuational contribution to the free energy.

The phase transition $D_{4h}^{17}\to D_{2h}^{18}$ takes place when $\tilde{u}+\tilde{v}>0,\tilde{v}<0$ while the transition to the D_{4h}^{16} phase is possible if $\tilde{u}+\frac{1}{2}\tilde{v}>0,\tilde{v}>0$ here

$$\tilde{u}=u-\frac{2\,\alpha^2C_{33}+\beta^2(C_{11}+C_{12})-4\alpha\beta C_{13}}{2[(C_{11}+C_{12})-2\,C_{13}^2]}+\frac{\gamma^2}{2\,C_{66}}.$$
$$\tilde{v}=v-\gamma^2/C_{66} \qquad (16)$$

The model parameters can be estimated from the microscopical calculations done in [18]. Therein the energy of the La_2CuO_4 lattice was calculated as a function of oxygen ion displacements These calculations were performed on the basis of the local density approximation. Comparing the parameters of the double-well potential presented in [18] with $F(T=0)$ in (15) we get

$$u\approx 423\ \mathrm{mev}^3,\quad V\approx -246\ \mathrm{mev}^3 \qquad (17)$$

The strain interaction constants α,β,γ in (15) can be estimated from experimental data [12],

$$\alpha\approx 3{,}7\ 10^{13}\mathrm{mev}^2,\quad \beta\approx 7{,}3\ 10^{12}\mathrm{mev}^2,\quad \gamma^2/C_{66}\approx 58\ \mathrm{mev}^3. \qquad (18)$$

Inserting (17),(18) we find out that $\tilde{v}<0$, $\tilde{u}+\tilde{v}>0$ i.e.for these parameters the HTT→LTO phase transition is realized.

4. Discussion

In the present paper, the microscopical model of the anharmonic lattice dynamics for $La_2Cu\ O_4$ in terms of rotational coordinates $R_\lambda(1)$ for octahedra CuO_6 has been proposed.The free energy (15) and the frequency of the soft tilting mode (14) were calculated to analyse structural phase transitions HTT→LTO→LTT. In the model apical oxygen displacements were explicitly taken into account, which resulted in new terms both in the anharmonic interaction ~ $\Gamma_2 R_x^2(1)R_y^2(1)$and in the interaction with an elastic strain ~$G_{66}R_x(1)R_y(1)\varepsilon_{xy}$unlike [13].These terms are important for estimation of the constants in the free energy expantion (15) because they determine the sequence of two SPT.

By estimating of the model parameters (17) from the microscopical theory [18] and by taking into account measurements [12] it has been shown that we may get only the SPT from the HTT→LTO phase. However, the second phase transition was observed in experiments [7,8] for Ba doped samples while for Sr doped ones it was not clearly seen.As far as electronic structures of Ba and Sr atoms are similar such difference can be accotiated only with the difference in ion radii:Ba(1,29A), Sr(1,10A) and La(1,04A). Their values are important for the determination of anharmonic constants: Γ_0,Γ_1 and $\Gamma_2$in our model. Especially, the strong anharmonic behaviour is observed for displacements of apical oxygens which

characterized by $\Gamma_2$constant. Supposing dependence of the Γ_2 and Γ_0,$\Gamma_1$constants on x we can get a change of the sign of v(x) to obtain $\tilde{v}>0$ or $\Gamma_2(x)>\Gamma_0(x)+\frac{1}{16}\Gamma_1(x)$ in (17).This x-dependence of the anharmonic constants was proposed in phenomenological model [14]. Therefore,to prove this consideration it is important to calculate the microscopical constants in doped system. In the case of doped materials one should also take into account electron-phonon interaction for holes on oxygen sites. This interaction is also important to describe the anomalies of electronic properties in LTT phase [8].

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Динамическая модель структурного фазового перехода в La_2CuO_4

Предложена микроскопическая ангармоническая модель динамики решетки кристаллов $La_{2-x}M_xCuO_4$ для описания мягкой ротационной моды, а также ее взаимодействия с деформациями. Вычислена свободная энергия и рассмотрены структурные фазовые переходы $D_{4h}^{17} \to D_{2h}^{18} \to D_{4h}^{16}$. Для описания этой последовательности фазовых переходов необходимо предположить сильную концентрационную зависимость констант ангармонизма.

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A Dynamical Model of Structural Phase Transition in La_2CuO_4

A microscopical model of anharmonic lattice dynamics for $La_{2-x}M_xCuO_4$ crystals is proposed to describe the soft tilting mode and its interaction with strains. The free energy for the model is calculated and the structural phase transition $D_{4h}^{17} \to D_{2h}^{18} \to D_{4h}^{16}$ are considered. It is proposed a strong x-dependence of anharmonic constants especially for apical oxygen displacements.

The investigation has been performed at the Laboratory of Theoretical Physics, JINR.

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